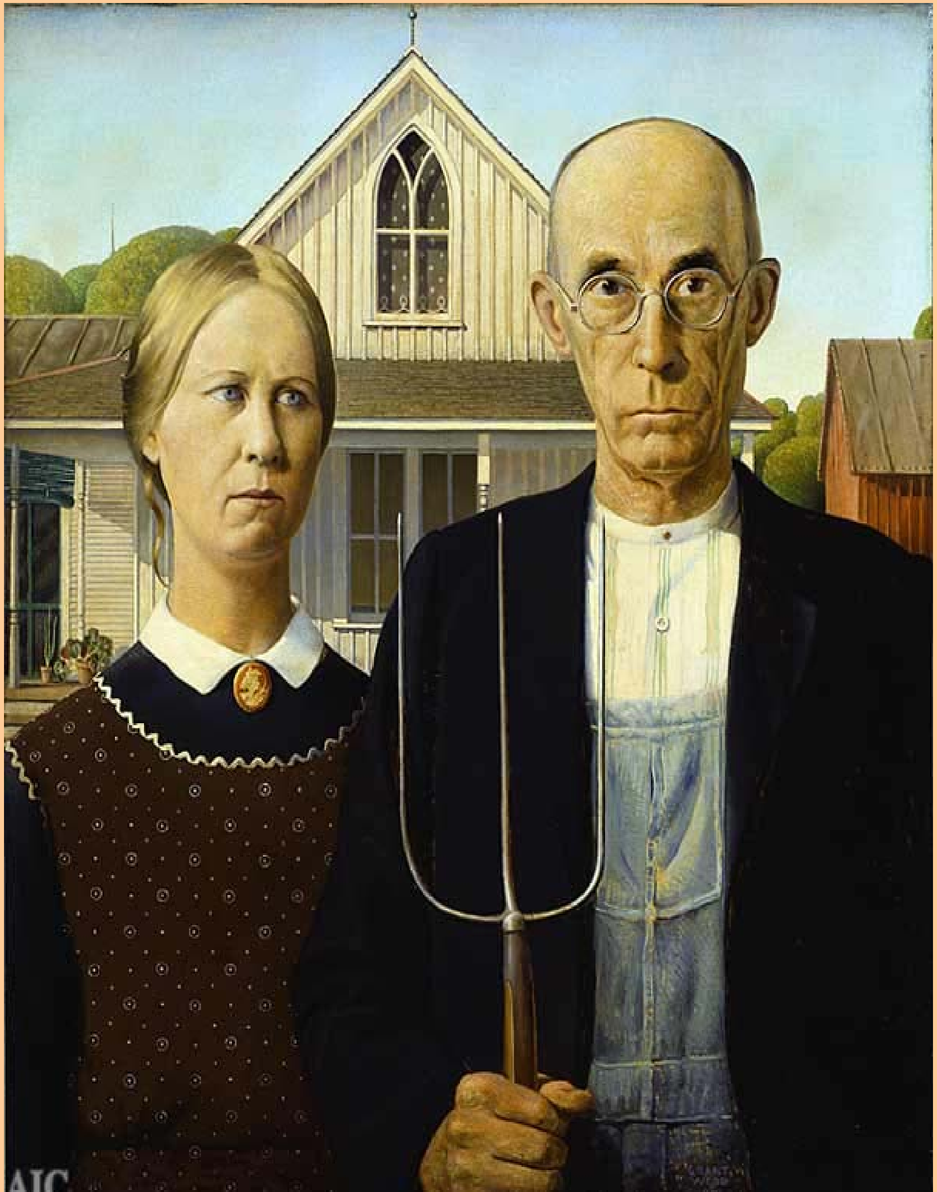

Farmers Know Best: Use of Laboratory Batch Tests To Evaluate Soil Leaching Concerns

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Basic Questions Considered

- How often does soil leaching drive risk-based site cleanups?
- Why does leaching to groundwater often drive soil cleanups?
- Are screening levels for leaching too conservative?
- Are site-specific data better than generic soil leaching models?
- Is there a recommended process?

How important is leaching?

I think we have a problem, Katherine

It depends upon several factors:

•Specific chemical involved

•Soil type

•Climate (annual rainfall)

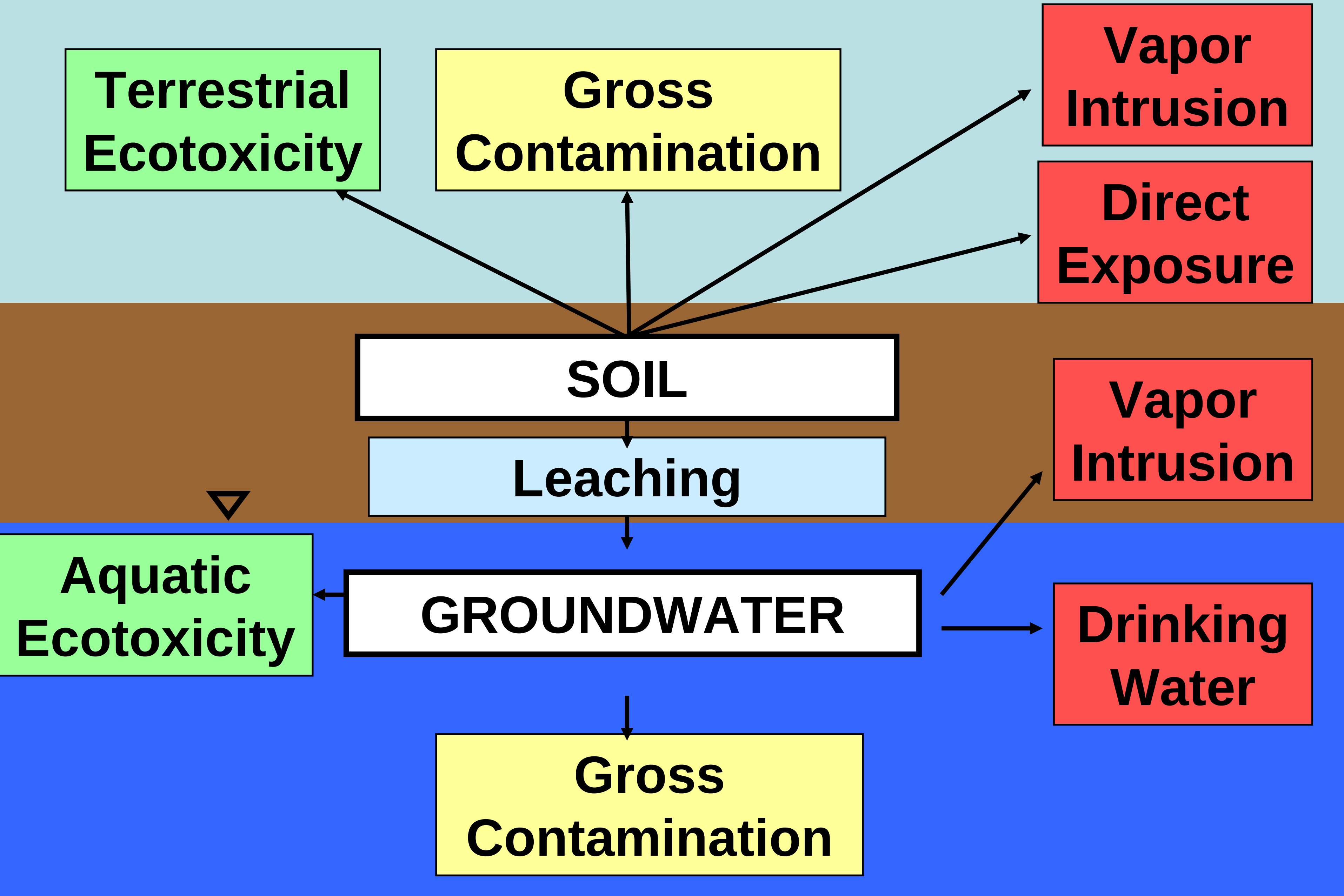
•Depth to groundwater

•Aquifer properties

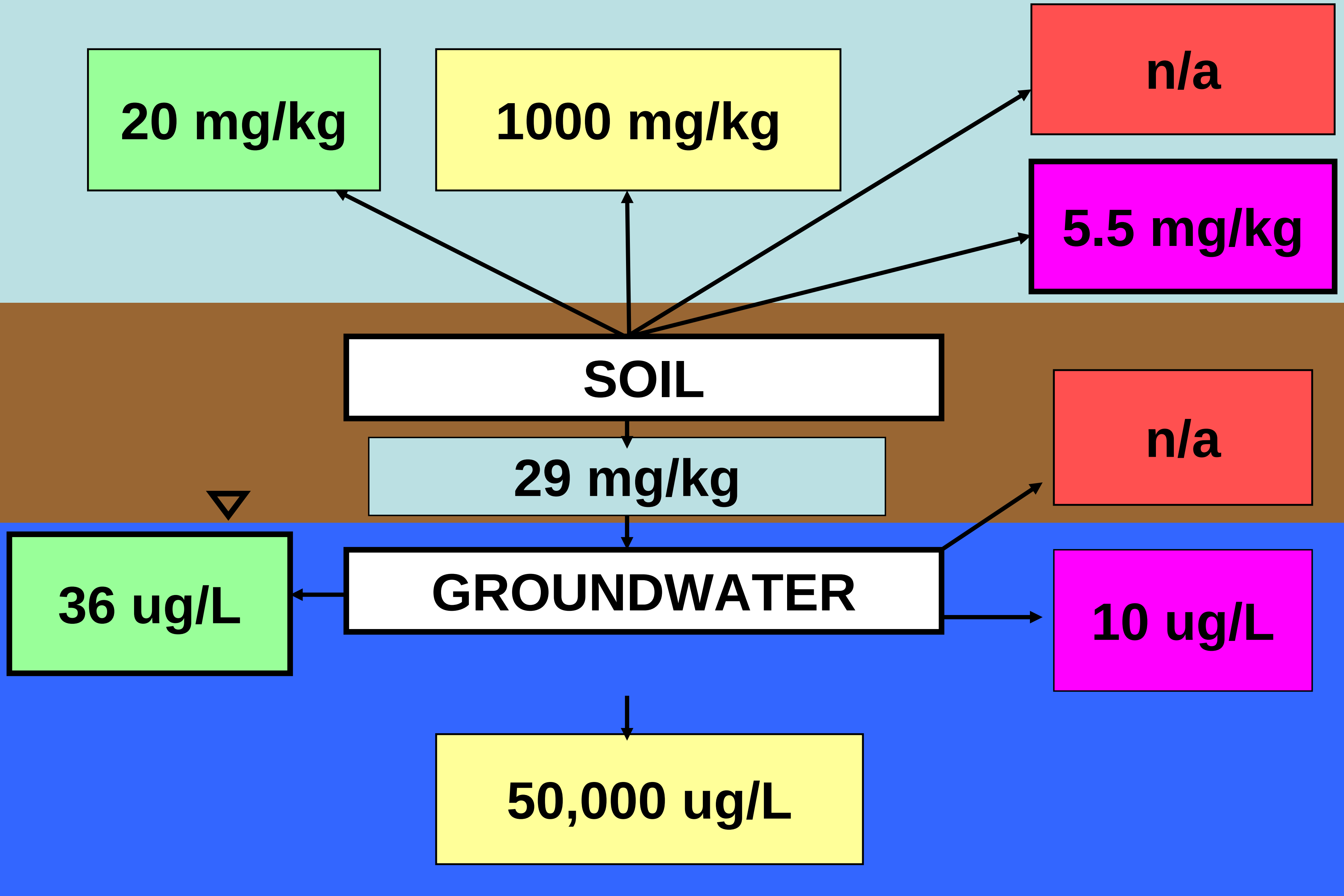
Contaminant Types & Primary Environmental Concerns

Chemical Type	Risk Driver
Carcinogenic metals, PAHs, PCBs, etc.	Direct Exposure (ingestion, absorption)
Carcinogenic VOCs	Vapor Emissions
Noncarcinogenic metals & pesticides	Terrestrial Ecotoxicity
TPH, phenols, aromatics	Gross Contamination
BTEX, chlorinated solvents, MTBE, inorganic salts	Leaching

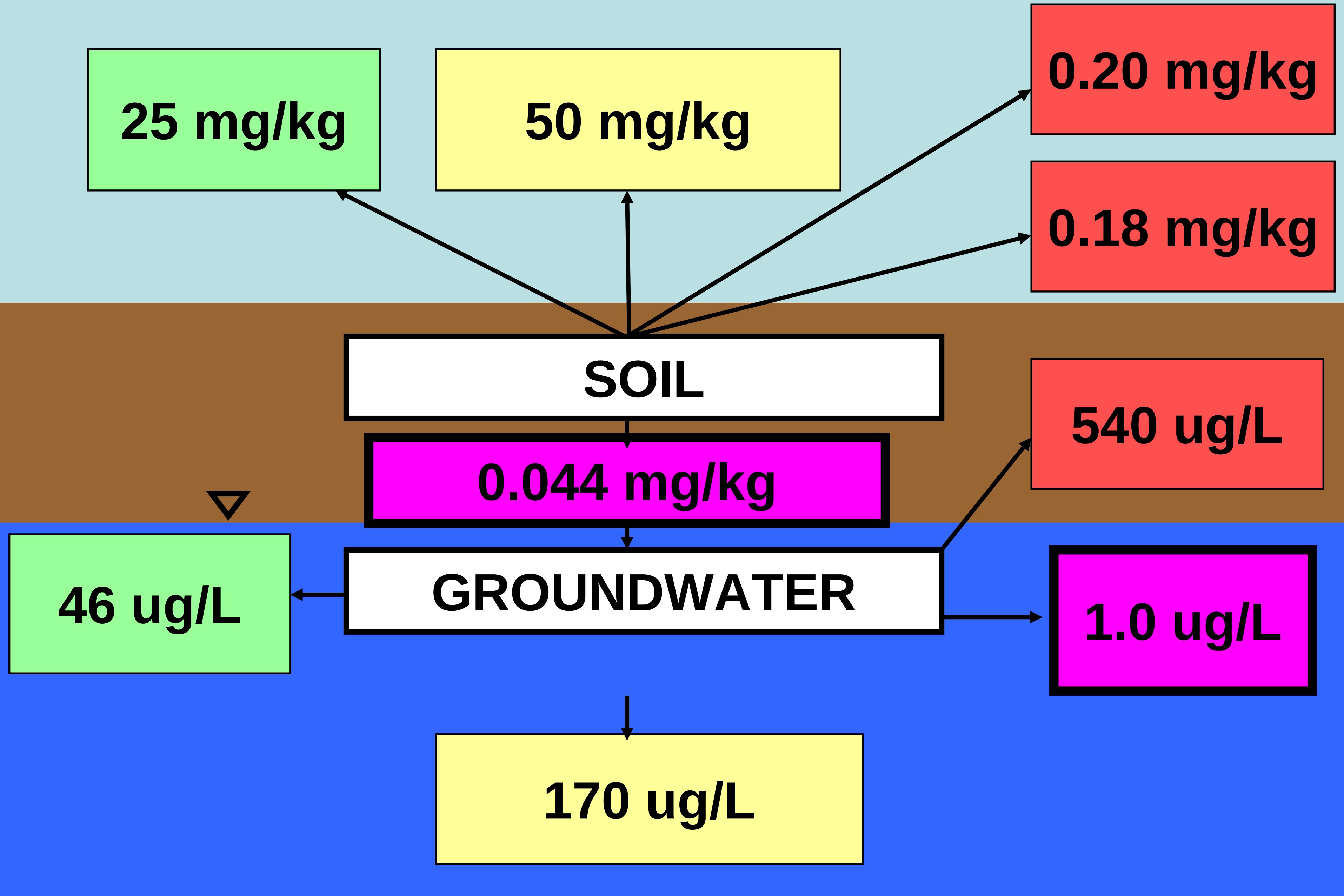
Primary Environmental Concerns



Arsenic

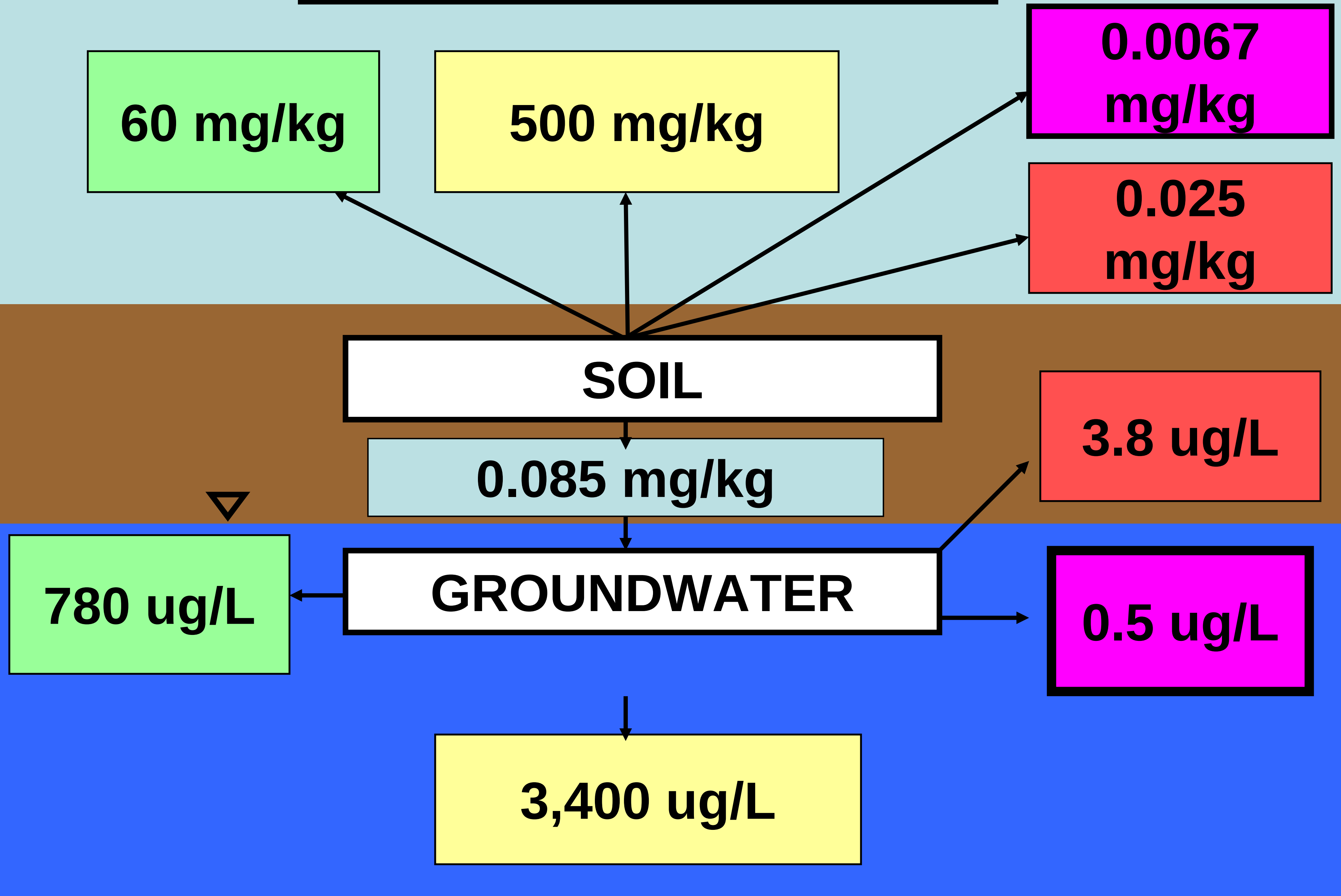

20 mg/kg
1000 mg/kg
n/a
5.5 mg/kg
SOIL
29 mg/kg
n/a
36 ug/L
GROUNDWATER
10 ug/L
50,000 ug/L

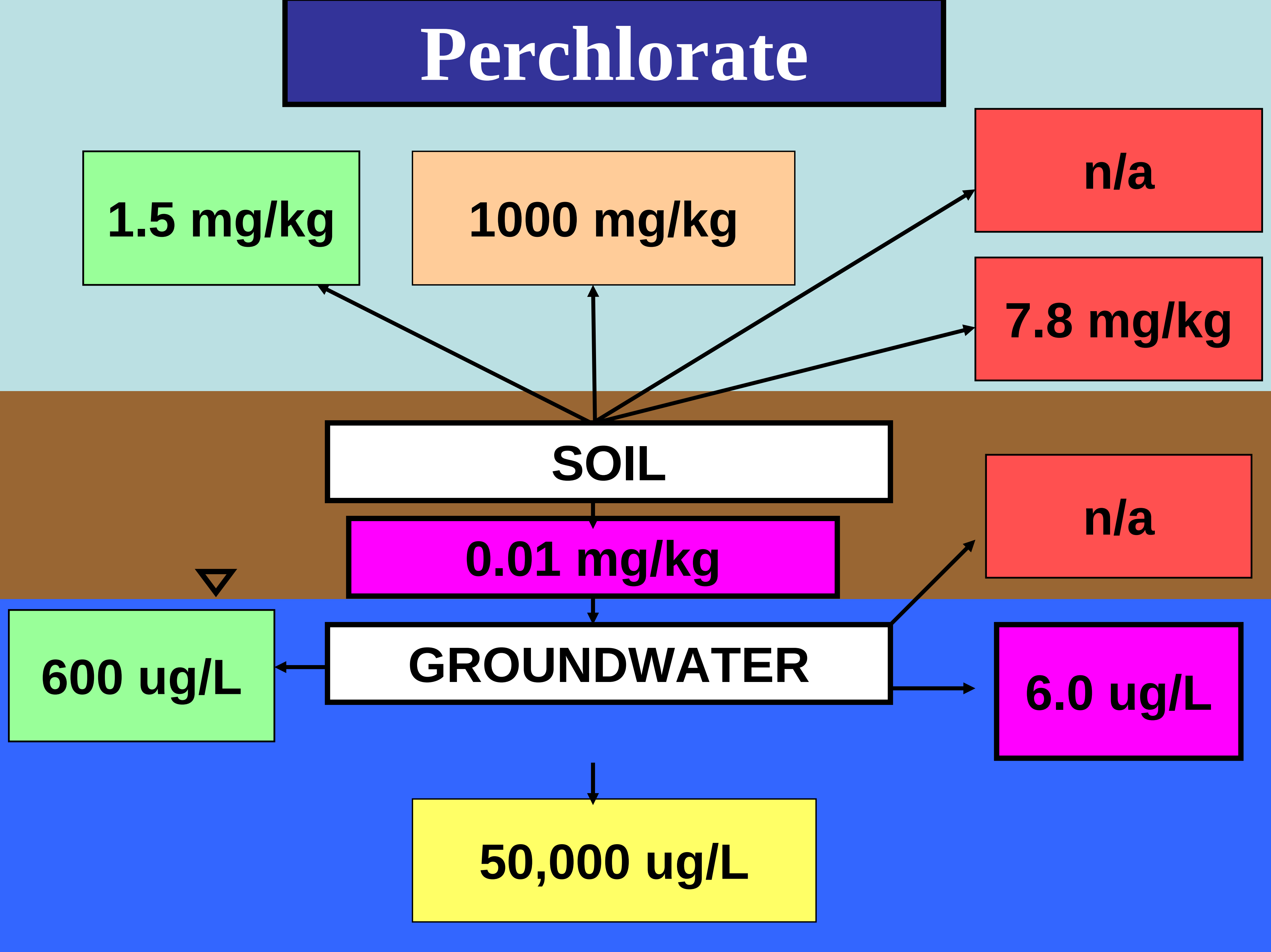
Benzene



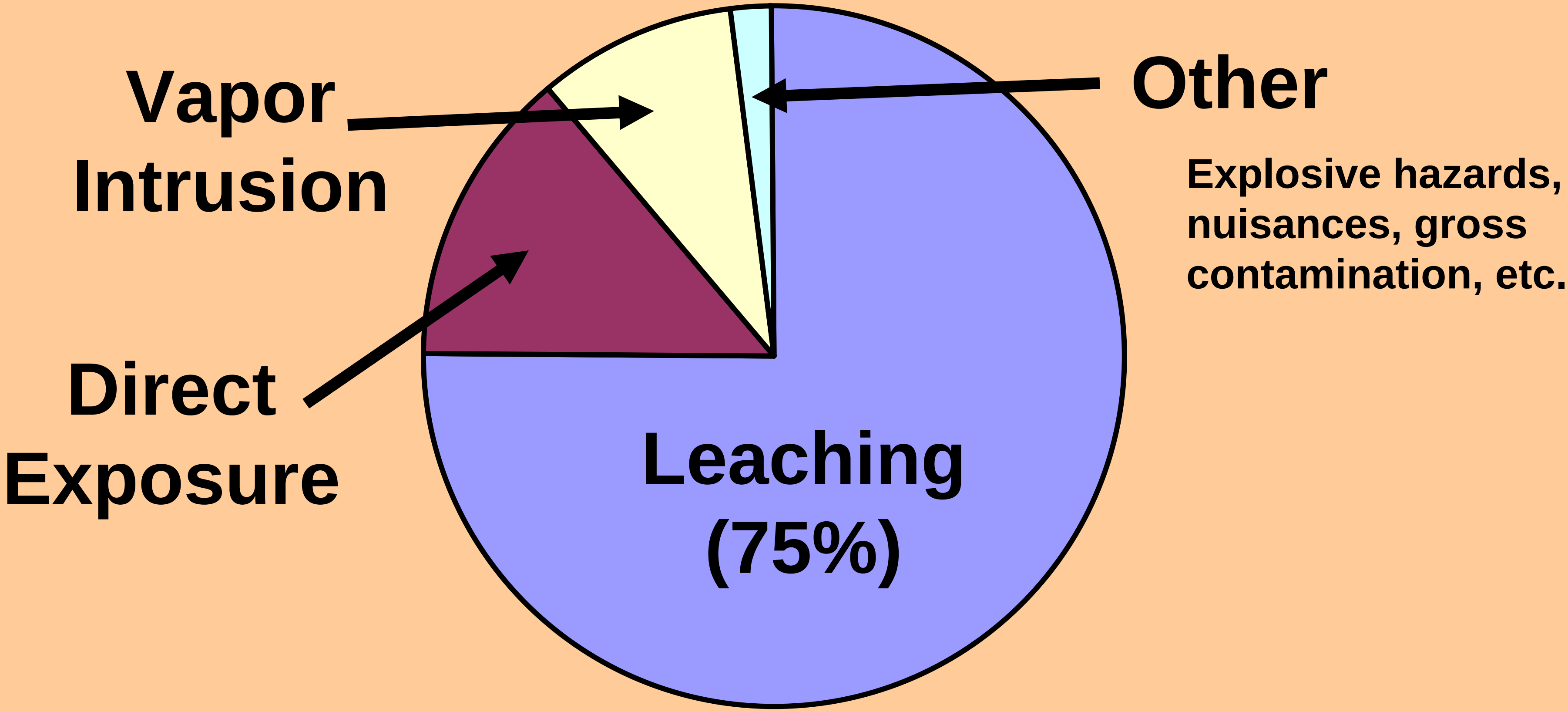
25 mg/kg
50 mg/kg
0.20 mg/kg
0.18 mg/kg
SOIL
540 ug/L
0.044 mg/kg
46 ug/L
GROUNDWATER
1.0 ug/L
170 ug/L

Vinyl Chloride




Perchlorate
1.5 mg/kg
1000 mg/kg
n/a
7.8 mg/kg
SOIL
n/a
0.01 mg/kg
600 ug/L
GROUNDWATER
6.0 ug/L
50,000 ug/L

Tier 1 Environmental Screening Levels "Risk" Drivers For Soil



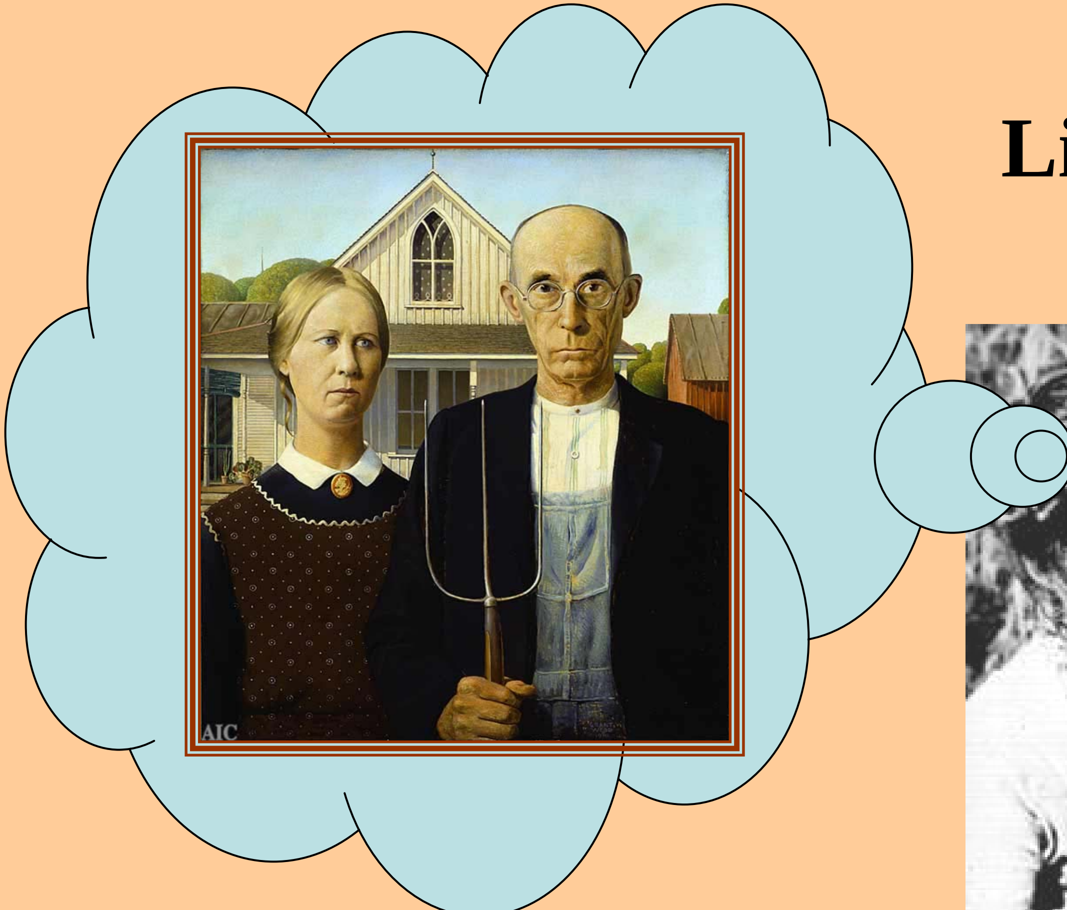
Why is this the case?

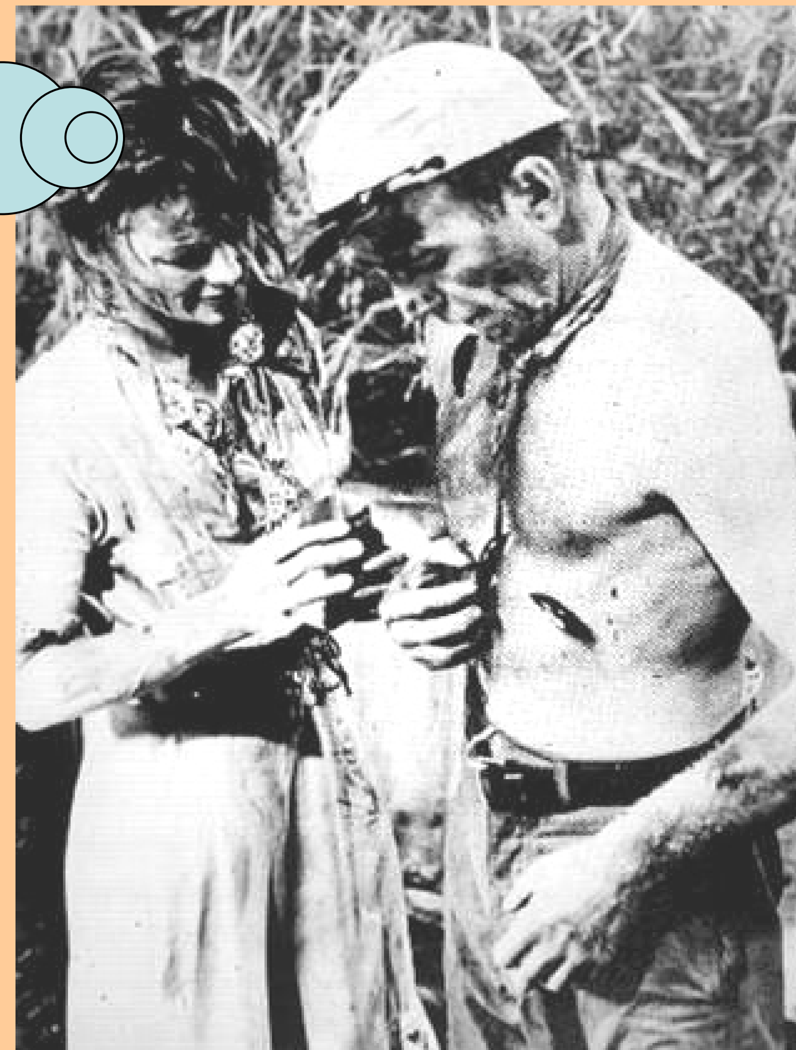
Are Leaching-Based Screening levels Too Conservative ?

Chemical	[1]USEPA R9 PRG *(mg/kg)*	*Leaching ESLs (mg/kg)*	
		CalEPA RB2	[2]USEPA SSG
TPH-g/d	1,600	100	25 to 100
Perchlorate	7.8	0.010	0.010
Benzene	0.53	0.044	0.004
Diuron	120	1.4	0.1

1. Residential direct exposure (TPH based on PRG model)
2. USEPA Soil Screening Guidance leaching model

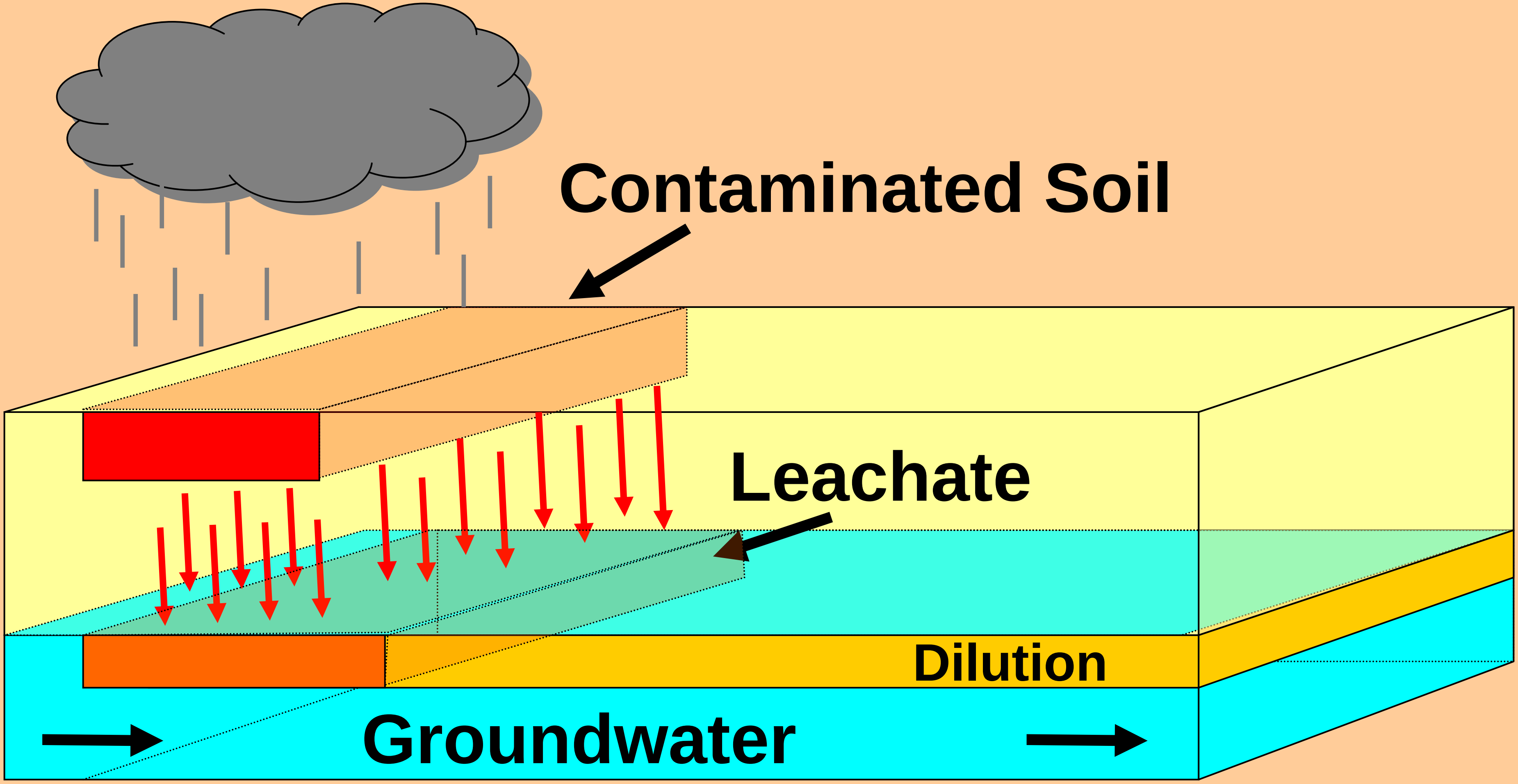
Listen to the farmers





Agricultural researchers have been studying pesticide leaching for decades.

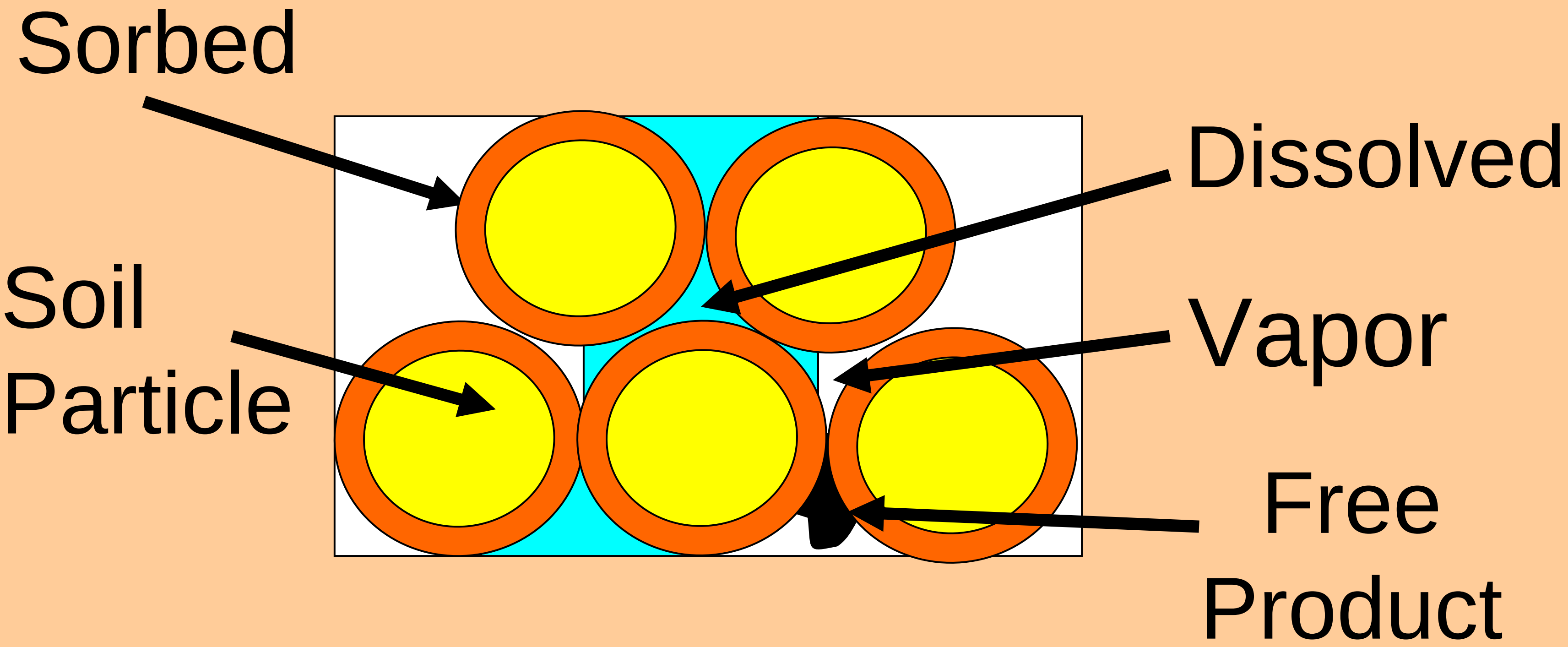
The basics of leaching…



GW Concentration = Leachate Conc. /DF

DF = GW Volume / Leachate Volume

Contaminant partitioning in soil



Sorption Coefficient:

Kd = Sorbed Conc./Dissolved Conc.

Default Partitioning in Soil

	*Percent Total Mass		
Chemical	**Sorbed**	**Dissolved**	**Vapor**
Arsenic	99+%	0.0004%	0%
TPH-diesel	98%	2%	<1%
Benzene	30%	50%	20%
Vinyl Chloride	6%	30%	64%
Perchlorate	0%	100%	0%

***Assuming USEPA default Kds and soil parameters**

Leaching potential

- Desorption isn’t just the reverse of sorption
- Desorption often slower than sorption
- Sorption tends to increase over time
- Described by partitioning coefficient Kd*

Estimating Leaching Potential

Equilibrium Partitioning Equation

$$C\ \text{leachate} = \frac{\text{Total Soil Concentration}}{(\text{Kd* + soil parameters})}$$

$$C_{leachate} = C_{total} \div \left(\left(Kd + \left(\frac{\theta_w + (\theta_a \times H')}{\rho b} \right) \right) \times \left(\frac{1mg}{1000\ \mu g} \right) \right)$$

Contaminant Mobility

- **Site-specific Kd* (& mobility) is a function of the chemical and the soil type**

- ***Soil factors:***

clays w/ high TOC	↑	**low mobility**
clays w/ low TOC		
silts		
sands	↓	**high mobility**

- ***Chemical factors:*** **solubility in water**
  valence state
  molecule size

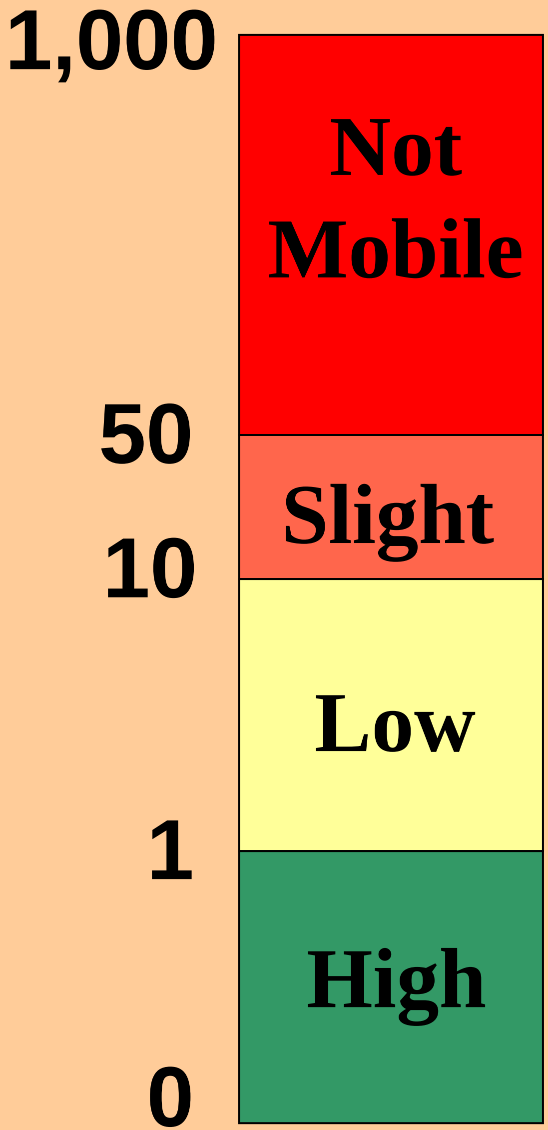
Contaminant Mobility

- Lower Kd = higher mobility
- Default Kd (organics) = koc x foc
- Kd >20: Immobile. Not a leaching threat
- Kd <20: Potentially mobile. Must be evaluated for leaching potential

(After Fetter 1988, Applied Hydrogeology)

Predicting Mobility based on Kd

Default Kd (foc = 0.1%)



Dioxin: 13,000

DDT, DDD, pyrene

chlordane, PCBs, arsenic

TPH, naphthalene, dieldrin

MTBE, perchlorate, benzene, chlorinated ethenes, ethanol

The Main Message:

- *Desorption* is critical factor
- Kd* controls mobility
  & concentration in leachate
- Need to know Kd* at your site
- How do you determine site-specific leaching potential?

Site-Specific Leaching Evaluations

- Laboratory batch tests based on real soil samples
- Synthetic precipitation leaching procedure (SPLP) or DI-wet test
- Can be easily obtained, not too expensive
- Probably yield better results than generic models

Estimating Kd* with Batch Tests (SPLP)

Step 1: Analyze soil sample for contaminant concentration

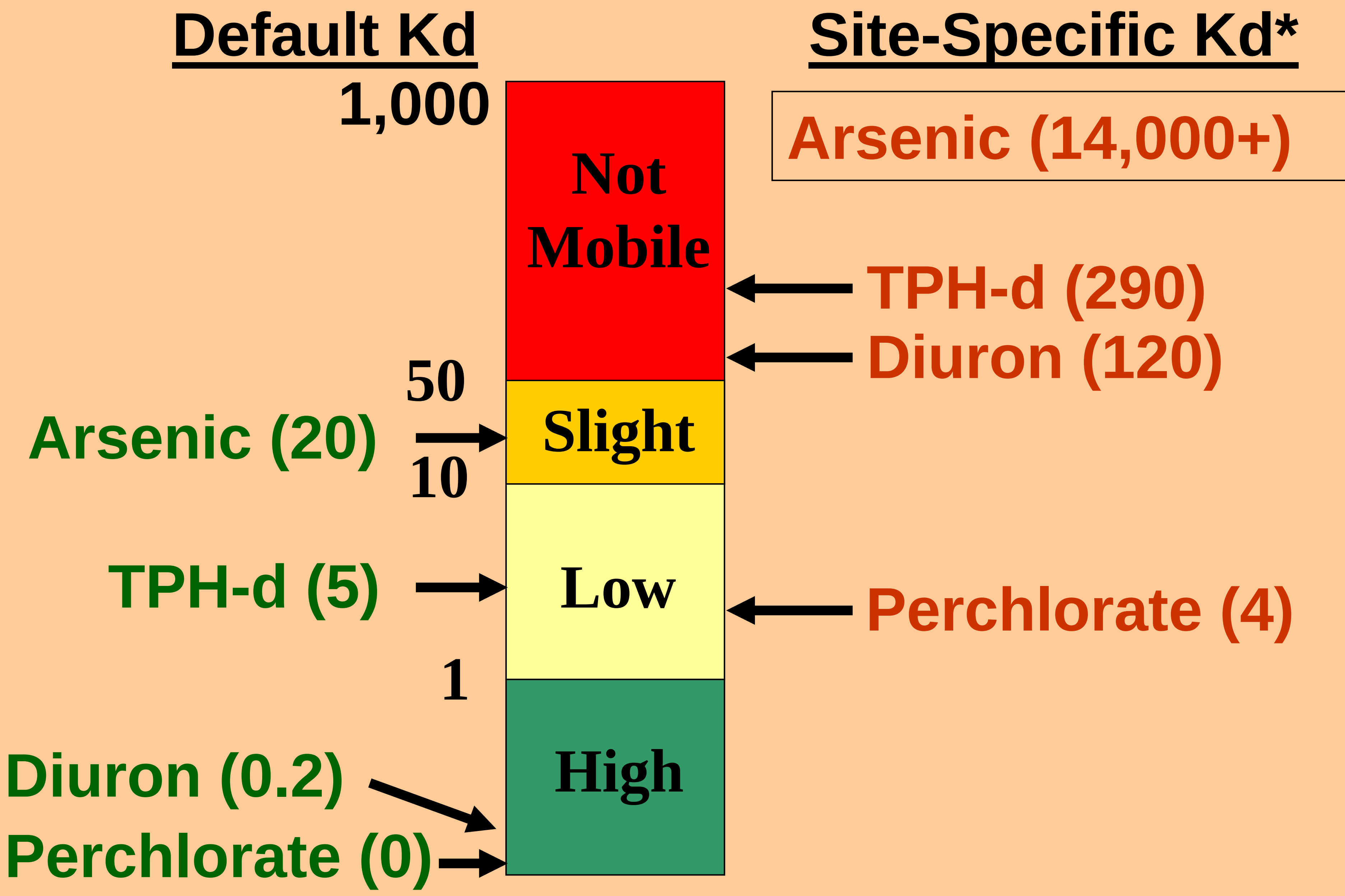
Step 2: Run SPLP test on split sample

- **Place 100 gram soil in 2 liters DI water (pH 5.5, 25° C)**
- **Remove airspace (especially for VOCs)**
- **Agitate 18 hours**
- **Analyze extract (leachate) for contaminants of concern**

Don’t directly compare SPLP data to ESLs!

Site Specific Batch Tests

- Results coming in from sites look very different from generic model predictions…


Default Kd
Site-Specific Kd*
1,000
Arsenic (14,000+)
Not Mobile
TPH-d (290)
Diuron (120)
50
Slight
Arsenic (20)
10
TPH-d (5)
Low
Perchlorate (4)
1
High
Diuron (0.2)
Perchlorate (0)

How Much Remains Sorbed?

Chemical	*Sorbed Fraction	
	Default	*SPLP data*
Arsenic	99.7%	99.9999%
TPH-diesel	98%	99.99%
Diuron	68%	99.9%
Perchlorate	0%	< 29%

Tier 1 Screening Levels vs Site-Specific Cleanup Levels

Chemical	*Tier 1 ESLs*	*Site-Specific Cleanup Goals*
Arsenic	**29 mg/kg**	**Not mobile @ 700+ mg/kg**
TPH-diesel	**100 mg/kg**	**Not mobile @ 1,000+ mg/kg**
Perchlorate	**0.010 mg/kg**	**~1.0 mg/kg ?**

Basic Questions Considered

- How often does soil leaching drive risk-based site cleanups?
- Why does leaching to groundwater often drive soil cleanups?
- Are screening levels for leaching too conservative?
- Are site-specific data better than generic soil leaching models?
- Is there a recommended process?

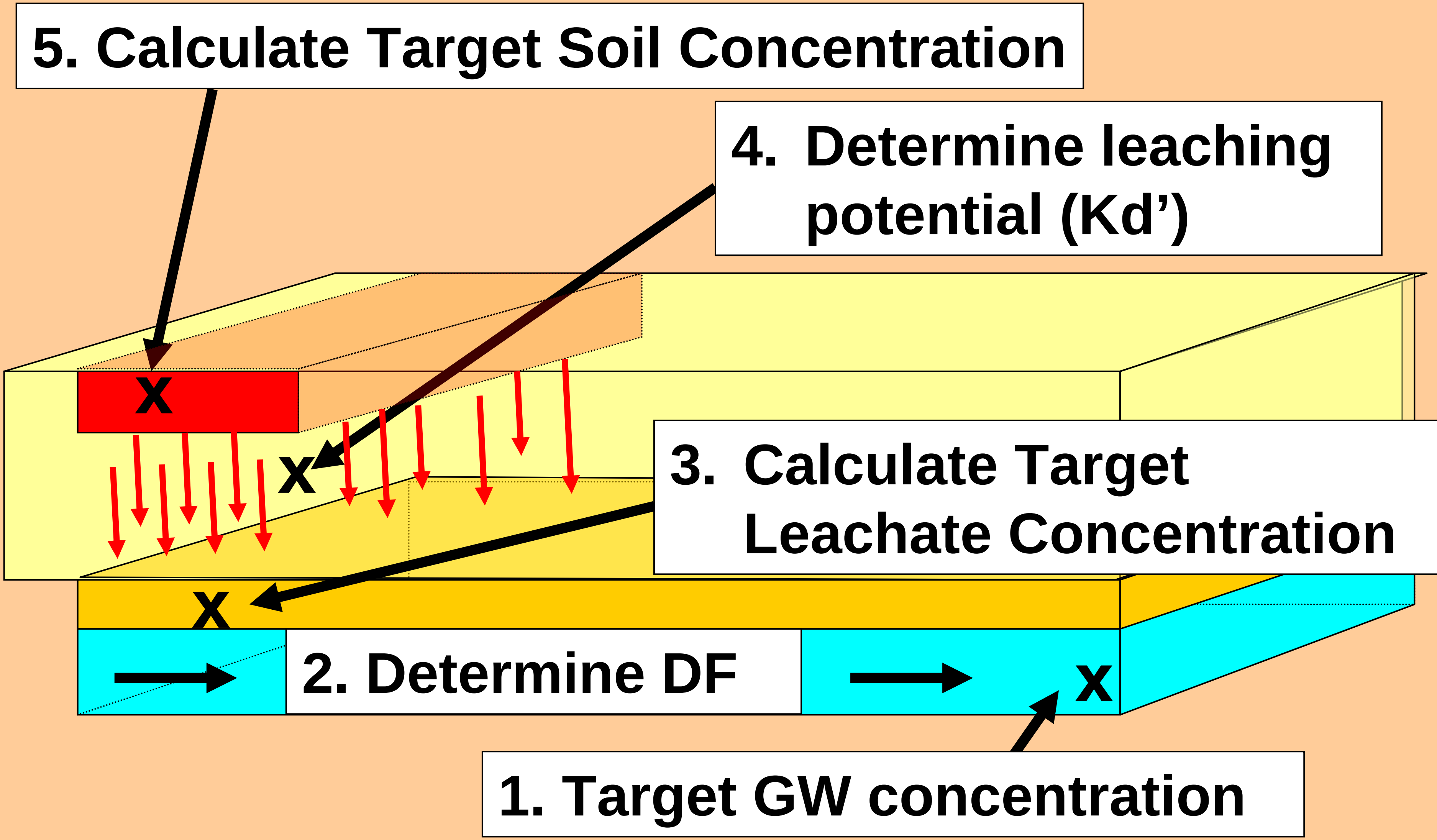
More Questions & Caveats

- Are SPLP results valid for highly volatile chemicals?
- What about effects of pH & redox on leaching of metals?
- Be careful of misuse of SPLP results

Example: Perchlorate Site

- California rocket motor manufacturing site
- Lots of perchlorate in groundwater
- Water cleanup standard set at 6 ppb
- Lots of perchlorate in soil (~360 kg)
- Soil perchlorate leaches into GW & SW
- Must remediate soils to protect water
- **What should the soil cleanup number be?**

Deriving a Soil Cleanup Goal

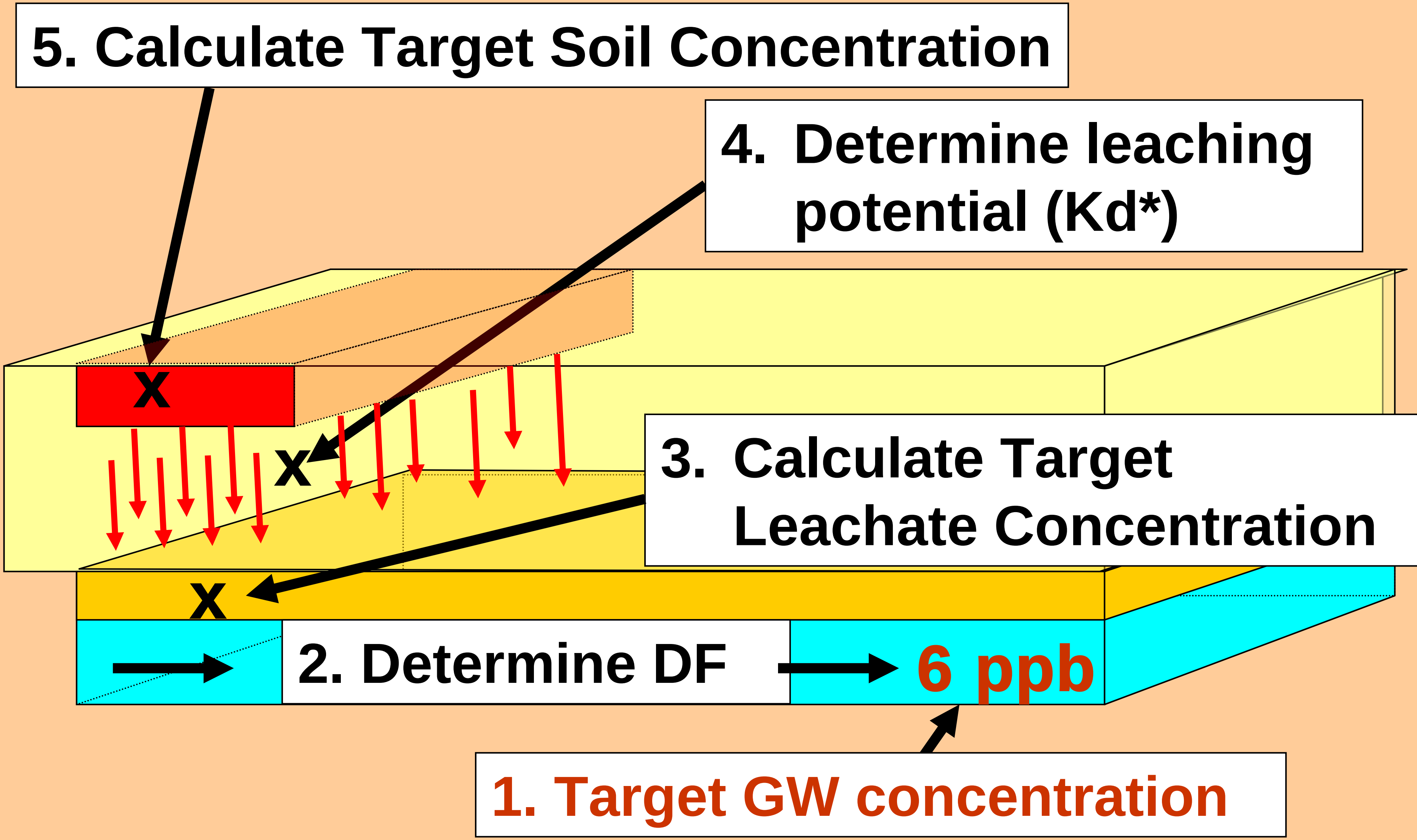


Deriving Target Soil Concentration

1. Start with the target groundwater concentration (e.g. MCL)
2. Determine dilution factor (DF).
3. Determine TLC. **TLC = TGC x DF**
4. Determine representative Kd*
5. Calculate target soil concentration

   TSC = TLC x [Kd* + (porosity/density)]

Deriving a Soil Cleanup Goal

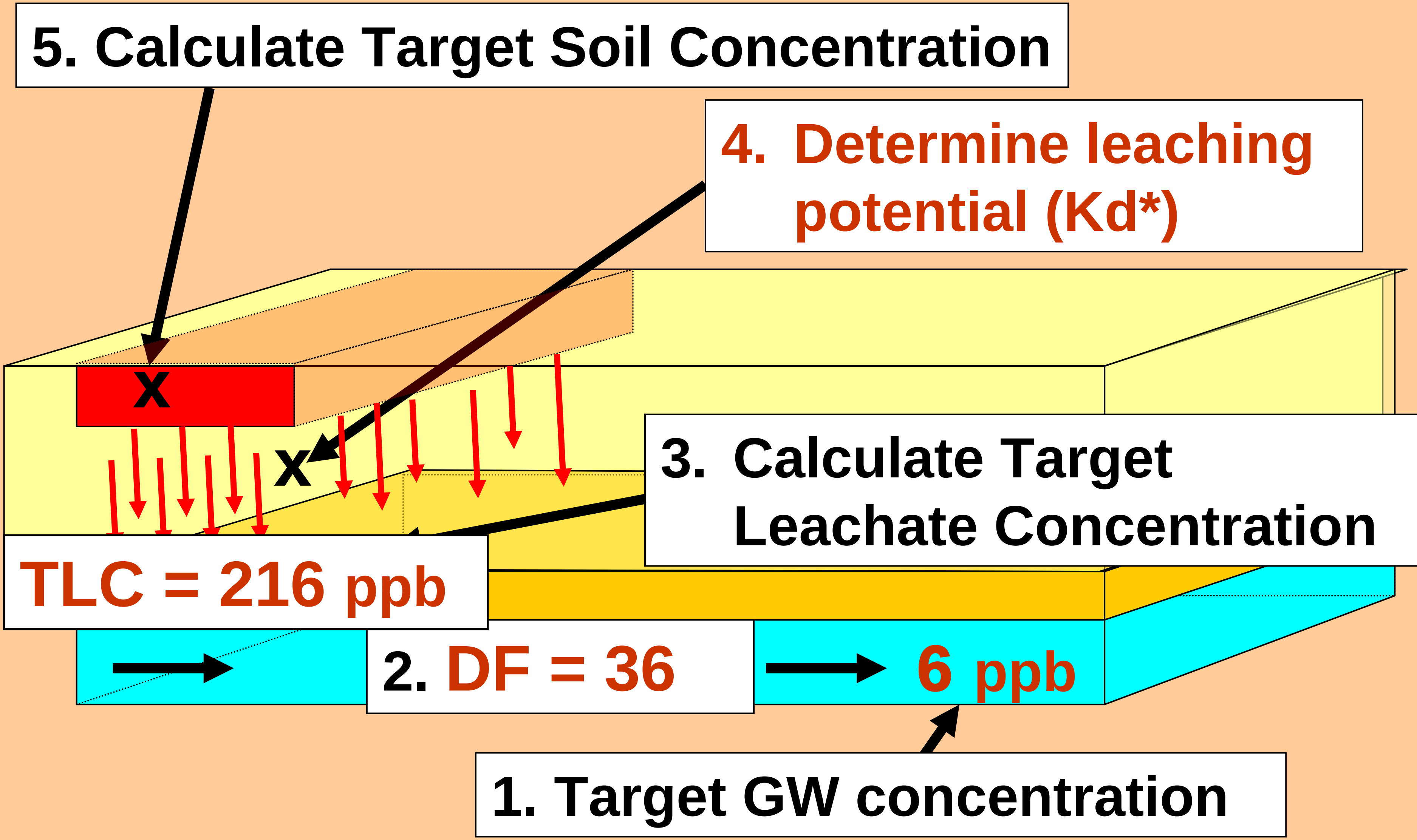


Deriving Target Soil Concentration

1. Start with the target groundwater concentration (**6 ppb**)
2. Determine dilution factor (DF). Using site data, **DF = 36***
3. Determine TLC. **TLC = TGC x DF**

TLC = 6 x 36 = 216 ppb

Deriving a Soil Cleanup Goal



Estimating Desorption Coefficient (Kd*) from SPLP Results

$$\mathbf{Kd^*} = \frac{\text{Mass still sorbed}}{\text{Mass in solution}} \times \frac{\text{Solute Mass}}{\text{Sample Mass}}$$

Mass still sorbed = original soil mass - mass in solution

$$Kd\ (\text{cm3/g}) = \frac{M_{solid}\,(\mu g)}{M_{solute}\,(\mu g)} \times \frac{1}{\text{Sample Mass(g)/Solute Mass(g)}} \times \left(\frac{1cm3}{1g}\right)$$

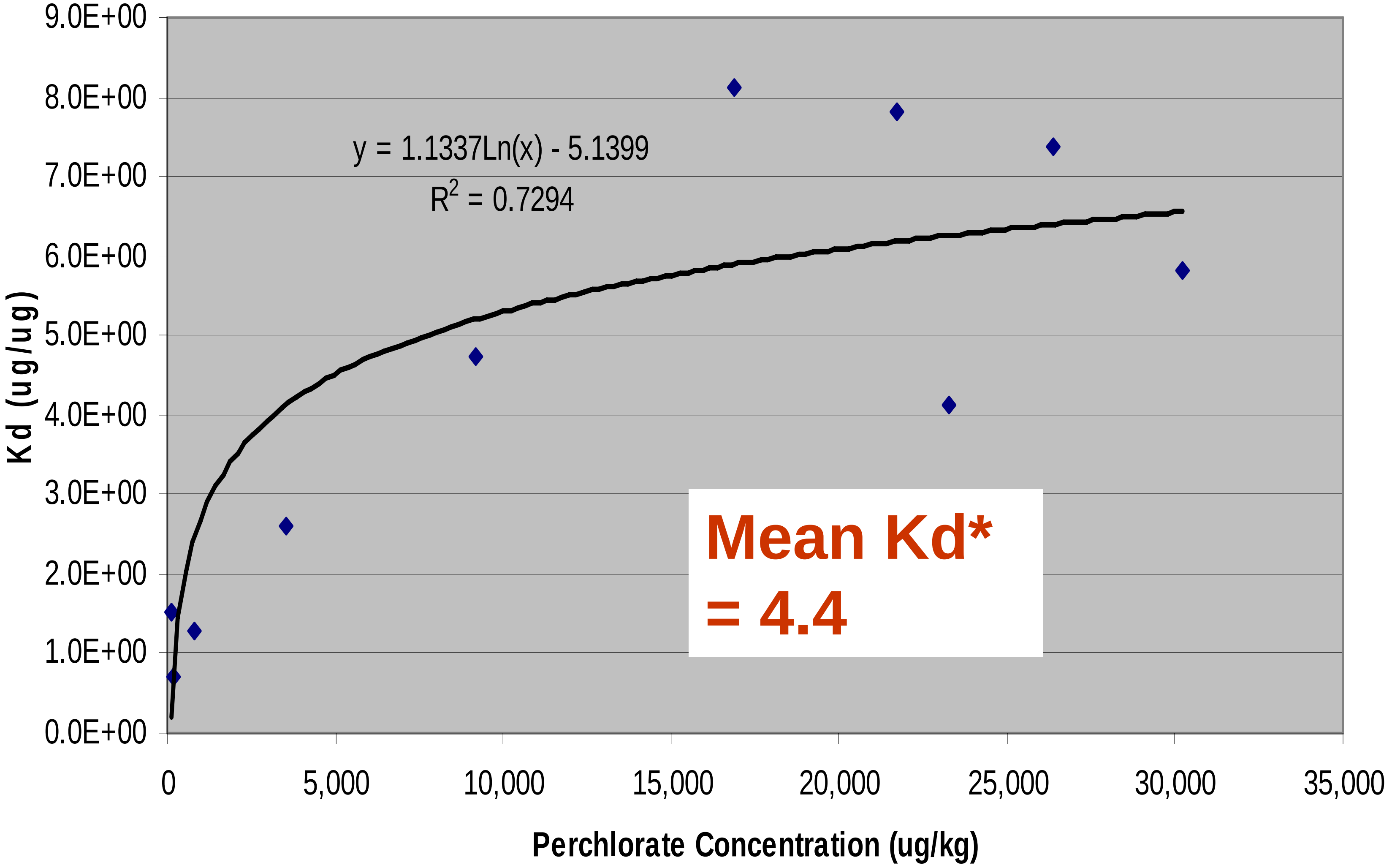
SPLP Results for Perchlorate

Perchlorate in Soil (ug/kg)	Perchlorate in Leachate (ug/L)	Percent Leached	Kd*
112	61	93	**1.5**
205	210	97	**0.7**
779	500	94	**1.3**
3,550	1,200	88	**2.6**
9,180	1,800	81	**4.7**
16,900	2,000	71	**8.1**
21,700	2,700	72	**7.8**
23,300	5,300	83	**4.1**
26,400	3,400	73	**7.4**
30,200	4,900	76	**5.8**

SPLP Results for Perchlorate

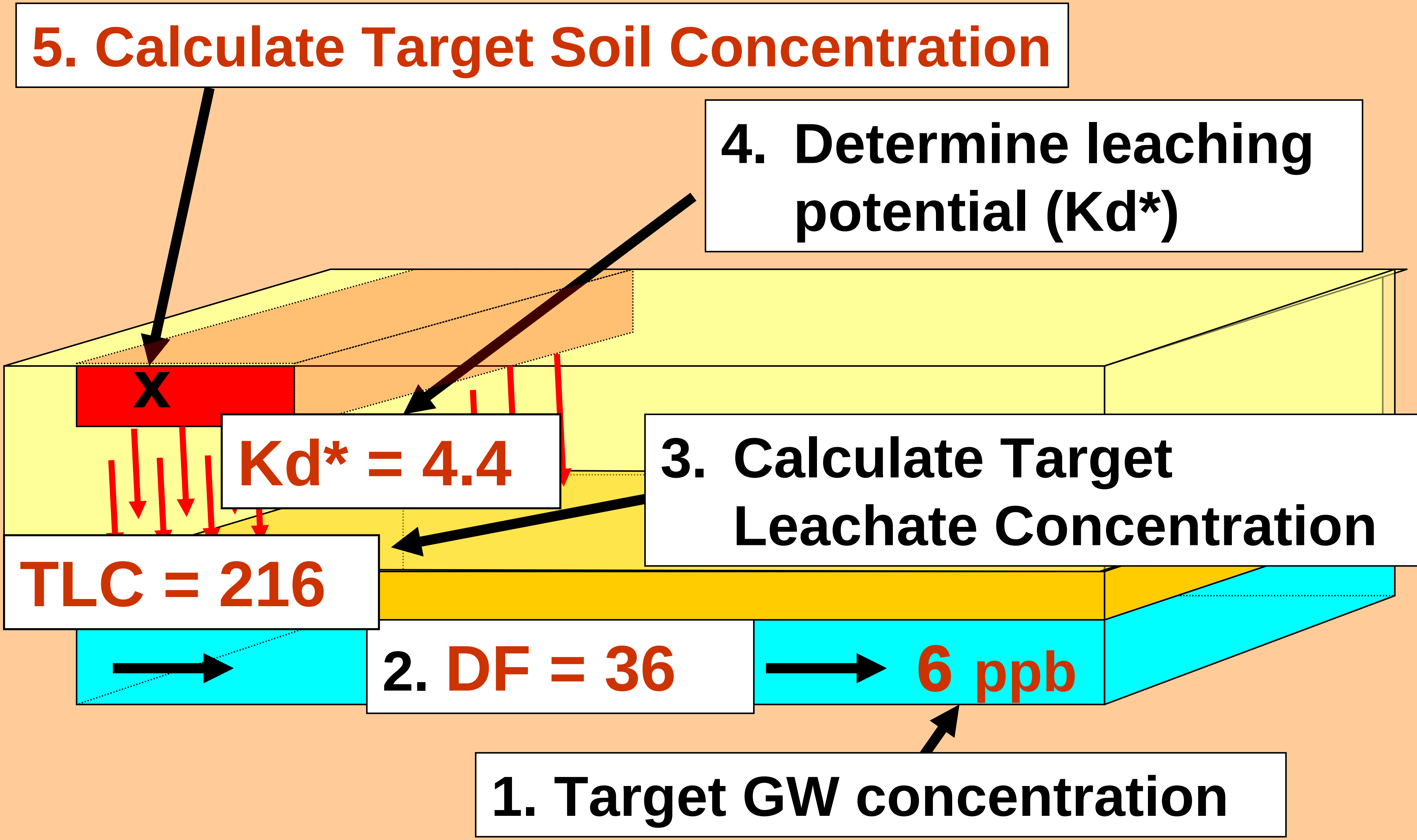
Perchlorate in Soil (ug/kg)	Perchlorate in Leachate (ug/L)	Percent Leached	Kd*
14	ND<3	0%	
5.5	ND<3	0%	
28	ND<3	0%	
33	ND<3	0%	
35	ND<3	0%	
45	ND<3	0%	
55	8	291%	
95	ND<3	0%	
422	25	117%	
240	6.2	52%	**19**

Calculated Perchlorate Kd values



Mean Kd* = 4.4

Deriving a Soil Cleanup Goal



Deriving Target Soil Concentration

1. Target GW concentration = **6 ppb**
2. Determine dilution factor. **DF = 36**
3. Determine TLC.

   TLC = TGC x DF = 216 ppb

4. Mean Kd* = **4.4**

5. Calculate Target Soil Concentration

TSC = TLC x [Kd* + (porosity/density)]

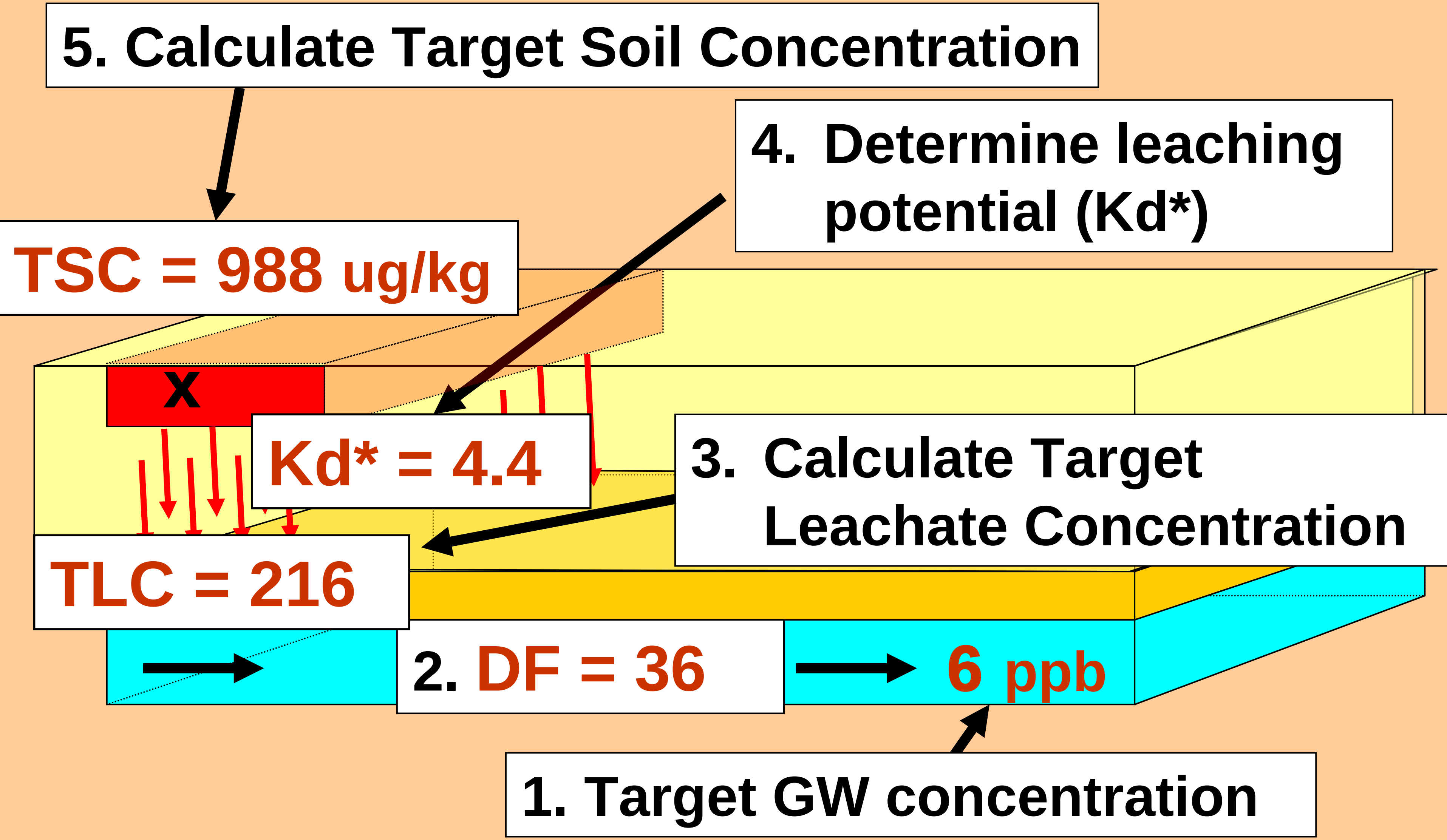
Deriving Target Soil Concentration

TSC = TLC x [Kd* + (porosity/density)]

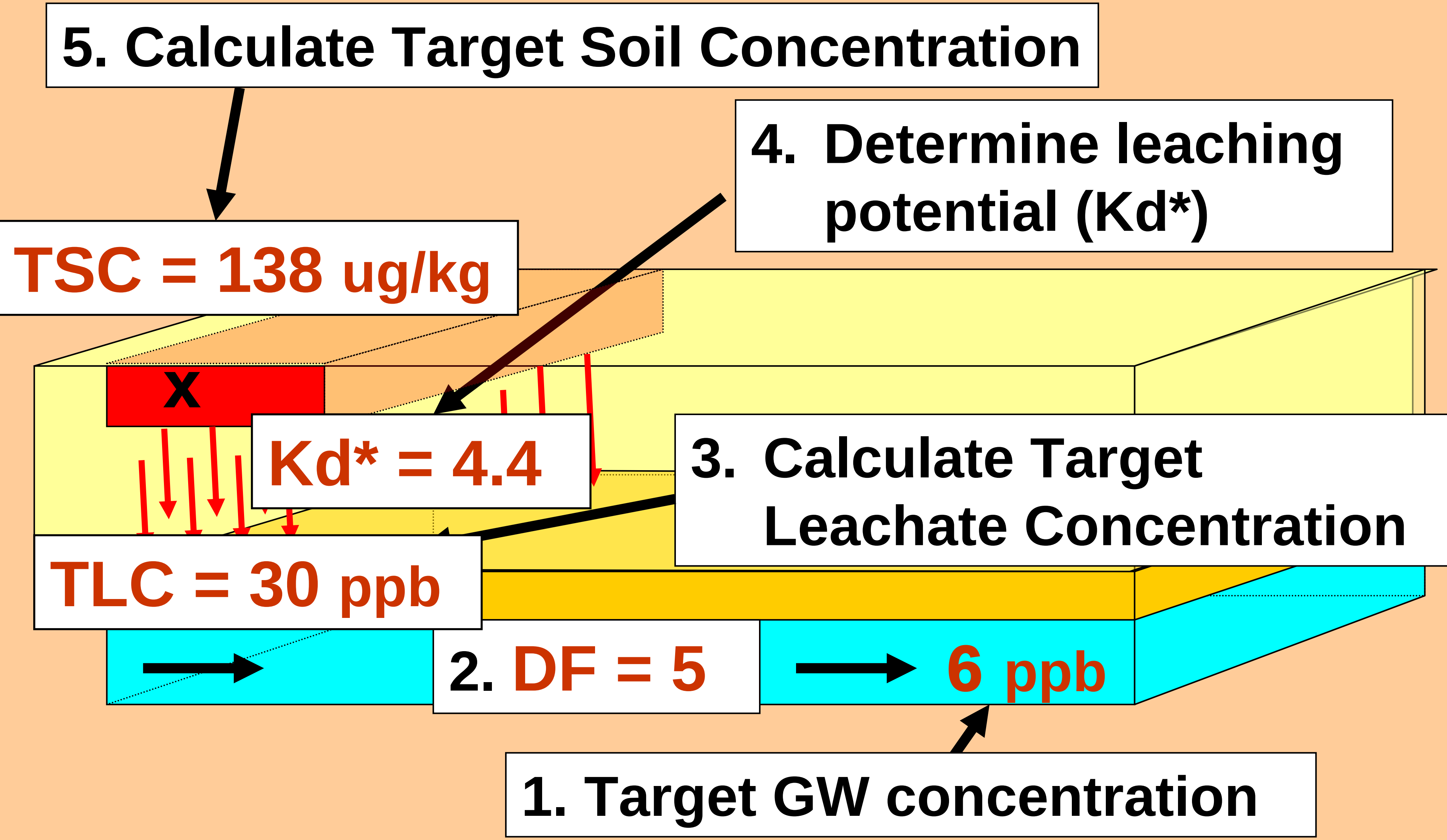
TSC = 216 x [4.4 + (0.35 / 1.80)]

TSC = 216 x 4.59 = 988 ug/kg

Deriving TSC, Subsurface Soils



Deriving TSC, Surface Soils



Next Steps

- Need a lot more site-specific leaching data! (more chemicals, more sites)
- Compile field-based Kd data for various contaminant groups
- Continue to evaluate the applicability of leaching tests for highly volatile organics
- Continue to improve leaching models by incorporating real site data
- Continue to optimize leaching ESLs

Getting out of the black box…

Simpler and better soil leaching models

Input:

- Minimize required input data
- Optional, default parameter values
- Site-specific “Kd”value(s)
- VOC vapor concentration

Output

- Initial concentration in leachate
- Travel time to groundwater
- Mass loss during transport
- Concentration at top of groundwater
- Concentration after mixing